

Non-Fermi liquid behavior in a fluctuating valence system, the filled skutterudite compound $\text{CeRu}_4\text{As}_{12}$

R. E. Baumbach, P. C. Ho, T. A. Sayles, and M. B. Maple

*Department of Physics and Institute for Pure and Applied Physical Sciences,
University of California at San Diego, La Jolla, CA 92093, USA*

R. Wawryk, T. Cichorek, A. Pietraszko, and Z. Henkie

*Institute of Low Temperature and Structure Research,
Polish Academy of Sciences, 50-950 Wrocław, Poland*

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Abstract

Electrical resistivity ρ , specific heat C , and magnetic susceptibility χ measurements made on the filled skutterudite $\text{CeRu}_4\text{As}_{12}$ reveal non-Fermi liquid (NFL) T - dependences at low T , i.e., $\rho(T) \sim T^{1.4}$ and weak power law or logarithmic divergences in $C(T)/T$ and $\chi(T)$. Measurements also show that the T - dependence of the thermoelectric power $S(T)$ deviates from that seen in other Ce systems. The NFL behavior appears to be associated with fluctuations of the Ce valence between 3^+ and 4^+ rather than a typical Kondo lattice scenario that would be appropriate for an integral Ce valence of 3^+ .

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I. INTRODUCTION

The filled skutterudite compounds of the form MT_4X_{12} where M = alkali metal, alkaline earth, lanthanide, actinide, $T = \text{Fe, Ru, Os}$ and $X = \text{P, As, Sb}$ have been shown to exhibit a wealth of strongly correlated electron phenomena including; spin fluctuations, itinerant ferromagnetism, local moment ferromagnetism and antiferromagnetism, conventional BCS superconductivity, unconventional superconductivity, heavy fermion behavior, and non-Fermi liquid behavior.^{1,2} Many of these phenomena depend on hybridization between the rare earth or actinide f - electron states and the conduction electron states. This trend is evident in the CeT_4X_{12} systems, for which the expected lattice constant value due to the Ln^{3+} lattice contraction at room temperature is strongly depressed for the phosphides, is not depressed at all for the antimonides, and is intermediate for the arsenides.^{3,4} The affects of hybridization are particularly dramatic for $CeRu_4Sb_{12}$ which, until now, was the only filled skutterudite known to show non-Fermi liquid (NFL) behavior.^{5,6,7} In this compound, the NFL behavior is characterized at low T as follows : resistivity - $\rho(T) \sim T^{1.4}$, specific heat divided by temperature - $C(T)/T \sim -\ln T$ or $T^{-0.58}$, and magnetic susceptibility - $\chi(T) \sim T^{-0.35}$, all of which suggest that $CeRu_4Sb_{12}$ is located near a quantum critical point (QCP). The value of the lattice constant for $CeRu_4Sb_{12}$ at room temperature indicates that the Ce ions are nearly trivalent, suggesting a Kondo lattice is the appropriate description of the physics. However, it should be noted that the unusual evolution of $\chi(T)$ with T signals a more complicated scenario where the Ce ions may undergo a continuous valence transition from 3^+ towards 4^+ with decreasing T .

In this paper, we report NFL behavior in the filled skutterudite $CeRu_4As_{12}$, indicating that this compound is also near a QCP. However, in this case, the lattice constant at room temperature and the T dependence of $\chi(T)$ reveal that the Ce ions have an intermediate valence between 3^+ and 4^+ . Therefore, $CeRu_4As_{12}$ is one of only a few compounds where the appropriate description of the NFL behavior may be a valence fluctuation rather than a Kondo lattice picture. We present measurements of $\rho(T)$, $C(T)$, $\chi(T)$, and thermoelectric power $S(T)$ for the compound $CeRu_4As_{12}$, characterize the NFL behavior, discuss the evidence for intermediate valence on the Ce ions, and compare to other Ce based systems where the NFL behavior may be related to intermediate Ce valence.

II. EXPERIMENT

Single crystals of $\text{CeRu}_4\text{As}_{12}$ were grown from elements with purities $\geq 99.9\%$ by a molten metal flux method at high temperatures and pressures, the details of which will be reported elsewhere.⁸ After removing the majority of the flux by distillation, $\text{CeRu}_4\text{As}_{12}$ single crystals of an isometric form with dimensions up to ~ 0.7 mm were collected and cleaned in acid in an effort to remove any impurity phases from the surfaces of the crystals. The crystal structure of $\text{CeRu}_4\text{As}_{12}$ was determined by X-ray diffraction on a crystal with dimensions of $0.17 \times 0.18 \times 0.23$ mm. A total of 5714 reflections (447 unique, $R_{\text{int}}=0.0772$) were recorded and the structure was resolved by the full matrix least squares method using the SHELX-97 program with a final discrepancy factor $R_1=0.0273$ [for $I > 2\sigma(I)$, $wR_2=0.0619$].^{9,10}

Electrical resistivity $\rho(T)$ measurements for $50 \text{ mK} < T < 290 \text{ K}$ were performed in a four-wire configuration in zero magnetic field using a conventional ^4He cryostat and a ^3He - ^4He dilution refrigerator. Magnetic susceptibility $\chi(T)$ measurements for $1.9 \text{ K} < T < 300 \text{ K}$ were conducted using a Quantum Design Magnetic Properties Measurement System (MPMS) on a mosaic of crystals ($m = 49 \text{ mg}$) which were mounted on a small Delrin disc using Duco cement. Specific heat $C(T)$ measurements for $650 \text{ mK} < T < 10 \text{ K}$ were made using a standard heat pulse technique on a collection of 11 single crystals ($m = 45 \text{ mg}$) attached to a sapphire platform with a small amount of Apiezon N grease in a ^3He semiadiabatic calorimeter. The thermoelectric power $S(T)$ for $0.5 \text{ K} < T < 350 \text{ K}$ of $\text{CeRu}_4\text{As}_{12}$ single crystals with length less than 1 mm was determined by the method described in ref.¹¹

III. RESULTS

Single crystal structural refinement shows that the unit cell of $\text{CeRu}_4\text{As}_{12}$ has the $\text{LaFe}_4\text{P}_{12}$ -type structure ($\text{Im}\bar{3}$) space group with two formula units per unit cell, and a lattice constant $a = 8.5004(4) \text{ \AA}$, in reasonable agreement with earlier measurements of $a = 8.4908 \text{ \AA}$ and $a = 8.4963 \text{ \AA}$.^{3,4,12} Other crystal structure parameters are summarized in Table I. The displacement parameter U_{eq} represents the average displacement of an atom vibrating around its lattice position and is equal to its mean-square displacement along the Cartesian axes. The displacement parameters determined for $\text{CeRu}_4\text{As}_{12}$ exhibit behavior

that is typical of the lanthanide filled skutterudites.^{13,14} Table I also indicates that the Ce and As sites in CeRu₄As₁₂ may not be fully occupied since there is $\sim 2\%$ uncertainty in the occupancy factors. The possible incomplete Ce or As occupancy is even more pronounced for some other crystals, not shown in table I, where the Ce and As filling deviates by as much as 3% from 100% occupation.

The T - dependence of the electrical resistivity is quite unusual (fig. 1). The large value of $\rho \sim 3.5$ m Ω cm at room temperature suggests that CeRu₄As₁₂ is a semimetal. Below 300 K, $\rho(T)$ decreases monotonically with decreasing T with negative curvature between 300 K and ~ 150 K, positive curvature from ~ 150 K to ~ 70 K, negative curvature between ~ 70 K and ~ 50 K, and a semi-linear region from ~ 50 K to ~ 10 K. At the lowest temperatures (65 mK $< T < 3.5$ K), $\rho(T)$ can be described by a power law of the form,

$$\rho(T) = \rho_0[1 + AT^n] \quad (1)$$

where $n = 1.4$, $A = 0.14$ K⁻ⁿ, and $\rho_0 = 136$ $\mu\Omega$ cm for nearly two decades in temperature. The power law behavior, illustrated in the inset to fig. 1, is consistent with that seen for other NFL systems.^{15,16,17} It should also be noted that no superconducting transition was detected above 65 mK.

Magnetic susceptibility $\chi(T)$ data likewise show an unusual T - dependence where $\chi(T)$ decreases with T down to ~ 90 K and then increases to low T (fig. 2). The decrease of $\chi(T)$ with decreasing T from ~ 300 K down to ~ 90 K is consistent with the Ce ions having an intermediate valence between 3⁺ and 4⁺. In this picture, the ratios $n^{3+}(T)$ and $n^{4+}(T)$ describe the fraction of Ce ions in each valence state. As temperature decreases, $n^{4+}(T)$ increases subject to the constraint $n^{3+}(T) + n^{4+}(T) = 1$. In the intermediate valence scenario, the 4f electron shell of each Ce ion fluctuates between the configuration 4f¹ (Ce³⁺) and 4f⁰ (Ce⁴⁺) at a frequency $\omega \approx k_B T_{vf}/\hbar$, where T_{vf} is a characteristic temperature separating magnetic behavior at high temperatures $T \gg T_{vf}$ and nonmagnetic behavior at low temperatures $T \ll T_{vf}$.^{18,19} For Ce³⁺, there is one localized 4f-electron and $\chi(T)$ should behave as a Curie-Weiss law modified by the CEF splitting of the ground state doublet and an excited state quartet by a splitting temperature $T_{CEF} \sim 100$ K. For Ce⁴⁺, there is no localized f-electron and $\chi(T)$ should behave as a Pauli susceptibility. However, for an intermediate valence state involving a temporal admixture of the 4f¹ and 4f⁰ configurations, $\chi(T)$ is expected to be intermediate between $\chi(T)$ of the Ce³⁺ and Ce⁴⁺ integral valence states for T

$\gg T_{vf}$ and to exhibit an enhanced Pauli-like susceptibility for $T \ll T_{vf}$. Magnetic ordering can also occur if the characteristic temperature for the RKKY interaction is comparable to the valence fluctuation temperature T_{vf} . Thus, down to 90 K, $\chi(T)$ in $\text{CeRu}_4\text{As}_{12}$ is consistent with an intermediate valence scenario, and one in which the intermediate valence shifts in the direction of 4^+ with decreasing T .

Below 90 K, $\chi(T)$ deviates from the typical intermediate valence scenario by exhibiting an upturn which persists down to 1.9 K. This behavior may indicate the onset of an unusual state below 90 K, or the presence of paramagnetic impurity ions. The upturn in $\chi(T)$ can be described by various functions at low temperatures, including a Curie law for $1.9 \text{ K} < T < 5 \text{ K}$ of the form,

$$\chi(T) = \chi_0 + \frac{C}{T} \quad (2)$$

where $\chi_0 = 1.5 \times 10^{-3} \text{ cm}^3/\text{mol}$ and $C = 4 \times 10^{-3} \text{ cm}^3\text{K}/\text{mol}$. Such a fit is consistent with the intermediate valence scenario suggested above, where χ_0 is the finite magnetic susceptibility of the intermediate valence state and the Curie component is due to the small fraction of remaining Ce^{3+} ions located at defect sites. Another possibility is that the low temperature Curie-like upturn is due to other magnetic rare earth impurities such as Gd^{3+} . From the value of the Curie constant obtained above, impurity concentrations equivalent to ~ 1500 ppm Ce^{3+} or ~ 500 ppm Gd^{3+} could account for the Curie contribution to $\chi(T)$. These concentrations seem rather large for paramagnetic impurities, and therefore suggest that the low temperature behavior is intrinsic to $\text{CeRu}_4\text{As}_{12}$. As shown below, the T - dependence of $\chi(T)$ below $\sim 10 \text{ K}$ is consistent with the NFL behavior observed in $\rho(T)$. For $1.9 \text{ K} < T < 10 \text{ K}$, $\chi(T)$ is described by either a power law or a logarithmic function (eqs. 3,4) where $m = 0.45$ and $a = 4.6 \times 10^{-3} \text{ cm}^3\text{mol}^{-1}\text{K}^m$, or $b = 4.2 \times 10^{-3} \text{ cm}^3/\text{mol}$ and $c = 1.2 \times 10^{-3} \text{ cm}^3/\text{mol}$, respectively (fig. 2).

$$\chi(T) = aT^{-m} \quad (3)$$

$$\chi(T) = b - c \ln(T) \quad (4)$$

Further analysis of $\chi(T)$ can be made by defining the effective moment $\mu'_{eff}(T)$ as shown in fig. 3,

$$\mu'_{eff}(T) \equiv \sqrt{\frac{3k_B\chi T}{N_A}} \quad (5)$$

Near 2 K, $\mu'_{eff} \sim 0.2 \mu_B$ is severely depressed from the free ion Hund's rule multiplet value $\mu_{eff}(\text{Ce}^{3+}) = 2.54 \mu_B$. This result strongly suggests that at low temperatures the Ce ions are in an intermediate valence state. The value of μ'_{eff} increases steeply up to 50 K, above which it increases more slowly to arrive at a value of $\mu'_{eff}(T) \sim 1.8 \mu_B$ near 300 K, which is still substantially reduced from the Ce^{3+} Hund's rule value. Therefore, it appears that throughout the entire temperature range measured, the Ce ions have a valence intermediate between 3^+ and 4^+

Displayed in fig. 4 are specific heat divided by temperature C/T vs T^2 data. For $T < 10$ K, the data decrease with temperature down to 2.6 K, below which there is an upturn that persists to 650 mK. It should be noted that a small feature with a maximum at 2.4 K is also observed. For temperatures $2.6 \text{ K} < T < 8 \text{ K}$, the data can be described by,

$$C/T = \gamma + \beta T^2 \quad (6)$$

where γ is the electronic specific heat coefficient and $\beta \propto \theta_D^{-3}$ describes the lattice contribution. Fits of eq. 6 to $C(T)/T$ show that $\gamma \sim 26 \text{ mJ/molK}^2$ and $\theta_D \sim 156 \text{ K}$. For $650 \text{ mK} < T < 2.6 \text{ K}$, C/T diverges from the T^2 T -dependence and increases with decreasing temperature. This low temperature divergence in C/T can be described by either a weak power law or a logarithmic divergence (eqs. 7,8) where $\varphi = 100 \text{ mJ/mol K}^{2-l}$ and $l = 0.76$ or $\phi = 101 \text{ mJ/mol K}^2$ and $\zeta = 84 \text{ mJ/mol K}^2$, respectively. Again, the behavior is consistent with typical NFL phenomena.

$$C/T = \varphi T^{-l} \quad (7)$$

$$C/T = \phi - \zeta \ln T \quad (8)$$

Fig. 5 shows the T -dependence of the thermoelectric power $S(T)$ for two samples of $\text{CeRu}_4\text{As}_{12}$. In the high temperature region, there is a two peak structure with a flat high temperature peak at $^hT_{max} = 250 \text{ K}$ which reaches $^hS_{max} = 67 \text{ V/K}$ and a sharper peak near $^lT_{max} \sim 75 \text{ K}$ which reaches a maximum value near $^lS_{max} = 66 \text{ V/K}$. The positions of the two peaks are sample independent and weakly sample dependent, respectively. Similar two peak structures have been observed for various other cerium systems including the heavy fermion system $\text{Ce}_x\text{Y}_{1-x}\text{Cu}_{2.05}\text{Si}_2$,²⁰ where $x = 0.3, 0.5$. In that case, the low- T peak is

ascribed to electron scattering by the ground state doublet of the Ce^{3+} ion while the high temperature peak is due to electronic scattering from the entire sextet of CEF levels of the Ce^{3+} ion. A more general description of $S(T)$ for the Ce-based intermetallic systems is given by a theoretical model that takes into account the CEF splitting of the Ce^{3+} 4f Hund's rule ground state multiplet and strong Coulomb repulsion of the 4f electrons.²¹ However, it is unclear how an intermediate valence picture should modify these behaviors.

The inset fig. 5i displays the T - dependence of $S(T)$ below 10 K. The sample with the lower thermoelectric power exhibits an abrupt step in $S(T)$ by about $\Delta S_{5K} \sim 2$ V/K near $T^* = 5.0$ K. The step results in a change of sign from positive above T^* to negative below. For the sample with higher $S(T)$, the jump at T^* is from one nearly linear $S(T)$ to another with a slightly lower slope. Additionally, a sign change at 0.9 K is observed for this sample. The $S(T)$ curves for these two samples converge at an upturn near $T = 0.47$ K, as shown in fig. 5(ii) where the average value of S/T is equal to -0.6 V/K². It is noteworthy that T^* coincides with the upper limit of the temperature range where the electrical resistivity is described by a power law with $n = 1.4$ (Fig. 1). Behnia et al.²² have argued that, in the zero temperature limit, the thermoelectric power should obey the relation,

$$q = \frac{SN_A e}{T\gamma} \quad (9)$$

where N_A is Avogadro's number, e is the electron charge and the constant $N_A e = 9.65 \times 10^4$ Cmol⁻¹ is the Faraday number. The dimensionless quantity q corresponds to the density of carriers per formula unit for the case of a free electron gas with an energy independent relaxation time. In our case, $q = -2.2$ and differs by sign from all eight cerium compounds considered in Ref.²² This unusual result may also be indicative of an NFL state at low temperatures.

IV. DISCUSSION

Taken together, measurements of $\rho(T)$, $\chi(T)$, $C(T)/T$, and $S(T)$ apparently reveal an anomalous NFL state for $\text{CeRu}_4\text{As}_{12}$ at low temperatures. The NFL behavior is characterized by sub-quadratic power law behavior in $\rho(T)$ and weak power law or logarithmic divergences in $\chi(T)$ and $C(T)/T$. The NFL phenomena are also evident in $S(T)$ which deviates from typical behavior previously observed for other Ce compounds and shows sample

dependence at low temperatures. To roughly quantify the NFL state, a temperature scale T_0 may be derived from the low temperature fits to $\rho(T)$, $\chi(T)$ and $C(T)/T$ using the scaled equations,^{16,17,18}

$$\rho(T) = \rho_0[1 + (T/T_{0\rho})^n] \quad (10)$$

$$\chi(T) = -B \ln(T/T_{0\chi}) \quad (11)$$

$$C(T)/T = -\lambda R/T_{0K} \ln(T/bT_{0K}) + \delta \quad (12)$$

which yield the values $T_{0\rho} \sim 4$ K, $T_{0\chi} \sim 30$ K, and $T_{0K} \sim 25$ K. For the fit to $C(T)/T$ (eq. 12), the parameters $\lambda = 0.251$ and $b = 0.41$ are taken from the two channel Kondo model which has proven to be a useful phenomenological description that yields reasonable values of the scaling temperature T_{0K} for many NFL systems, although is not strictly appropriate for the present situation. The unusual behavior seen in $S(T)$ below 5 K also supports the viewpoint that T_0 is in this temperature range.

A comparison to typical heavy fermion systems may also be made by computing an effective Wilson-Sommerfield ratio $R_W = (\pi^2 k_B^2 / 3\mu_{eff}^2)(\chi_0/\gamma)$. Since unambiguous choices for χ_0 and γ are not obvious, the values are taken at 1.9 K to probe the low temperature state. The Hund's rule effective magnetic moment $\mu_{eff} = 2.54 \mu_B$ for Ce^{3+} ions is also used. From these values, R_W is calculated to be ~ 0.5 . This value is similar to those found in f-electron materials that exhibit Fermi liquid behavior with heavy quasiparticles. However, the relationship between χ_0 and γ in an NFL system remains unclear.

In addition to NFL behavior, $CeRu_4As_{12}$ appears to be characterized by Ce ions with a valence intermediate between 3^+ and 4^+ . This observation is first suggested by the depressed room temperature lattice constant, as compared to the expected trivalent lanthanide contraction (LC) value for the MRu_4As_{12} series where $M = La - Pr$.^{3,4} To emphasize this point, a comparison can be made to the related compounds MT_4Sb_{12} and MT_4P_{12} where $M = La - Nd$ and $T = Fe, Ru, \text{ and } Os$. For MT_4Sb_{12} , there is no deviation from the expected LC value at room temperature and, therefore, the Ce ions appear to have a valence near 3^+ , although this does not preclude the possibility of an intermediate valence state below room temperature. This viewpoint is supported by XANES measurements of $CeFe_4Sb_{12}$ and $CeOs_4Sb_{12}$ where Ce is shown to be in the trivalent state at room temperature.^{23,24}

In contrast, MT_4P_{12} compounds follow a LC except in the case $\text{M} = \text{Ce}$ where the lattice constant is severely depressed from the expected value. In this case, XANES measurements show that the Ce ions in $\text{CeT}_4\text{P}_{12}$ ($\text{T} = \text{Fe}, \text{Ru}$) are mainly 3^+ with a small 4^+ contribution at room temperature.^{25,26} It should be noted that XANES measurements of Ce compounds may underestimate the 4^+ compared to the 3^+ component of the Ce valence.²⁷ Since the lattice constant suppressions for the $\text{CeT}_4\text{As}_{12}$ compounds are between that for the $\text{CeT}_4\text{Sb}_{12}$ and $\text{CeT}_4\text{P}_{12}$ systems, it is likely that the valence of their Ce ions are likewise intermediate.

The intermediate valence picture is further supported by the unusual T - dependence of $\chi(T)$ for $\text{CeRu}_4\text{As}_{12}$ which is similar to that seen for other intermediate valence compounds such as SmS , SmB_6 , or $\text{La}_{1-x}\text{Th}_x$ doped with Ce impurities where the Ce valence evolves from 3^+ to an intermediate value as a function of Th concentration.^{18,19,28,29} Moreover, by comparison to $\text{CeRu}_4\text{As}_{12}$, it appears that $\text{CeRu}_4\text{Sb}_{12}$ may also develop an intermediate valence state below room temperature.^{5,6,7} Although it appears that the Ce ions in $\text{CeRu}_4\text{As}_{12}$ have valence between 3^+ and 4^+ , additional characterization such as XANES measurements are required to verify this hypothesis. It should also be noted that a Kondo volume collapse scenario could, in principle, account for the reduced lattice constant.³⁰

In typical discussions of NFL physics in f-electron materials, the phenomena are described in terms of interactions between the itinerant electrons and the magnetic rare earth ions. Examples include; (1) nearness to various types of magnetic quantum critical points where a second-order phase transition is suppressed to 0 K and quantum fluctuations govern physical properties,^{31,32} (2) Kondo disorder where a range of Kondo temperatures are allowed including $T_K = 0$ K,^{33,34,35} (3) the Griffiths phase model,³⁶ and (4) the quadrupolar Kondo model.³⁷ These pictures have been moderately successful in describing numerous NFL systems.¹⁵

However, for the single crystal $\text{CeRu}_4\text{As}_{12}$ specimens reported here, Kondo scenarios are unlikely to describe the NFL behavior since they require the presence of Ce^{3+} ions and, as argued above, the Ce ions in this system appear to have a temperature dependant intermediate valence. As such, we suggest that $\text{CeRu}_4\text{As}_{12}$ lies near a QCP where valence fluctuations on the Ce ions give rise to the incipient NFL state. The existence of a QCP due to a quantum phase transition from integral to intermediate valence has been conjectured in a few other compounds, most notably CeCu_2Si_2 , CeCu_2Ge_2 , CePd_2Si_2 , and the alloy $\text{CeCu}_2(\text{Si}_{1-x}\text{Ge}_x)_2$.^{38,39,40,41,42,43} The low pressure region of the T - P phase diagram for these compounds is similar to that seen for heavy fermion superconductors such as

CeIn₃ and CeMIn₅ (M = Co, Rh) where antiferromagnetic order is suppressed with increasing pressure towards a QCP, around which a superconducting dome is observed at low temperatures.^{44,45,46} Higher pressures then tune the Ce ion from integral to intermediate valence, resulting in a second superconducting dome near a QCP associated with the valence transition. The region surrounding the superconducting dome maximum is also accompanied by NFL behavior. By comparison, an analogous description may be applicable for CeRu₄As₁₂.

It is also of note that a recent study shows that $\rho(T)$ for polycrystalline specimens of CeRu₄As₁₂ conforms to activated behavior $\rho \sim \exp(\Delta/T)$ where $\Delta = 50$ K while $\chi(T)$ and $C(T)/T$ are similar to those reported here.¹² The transition from a weakly insulating state for polycrystalline samples to semimetallic NFL behavior for single crystal samples further signals that CeRu₄As₁₂ is near a QCP and that its physical properties are tuned by some parameter, such as Ce filling or structural disorder, that is affected by sample growth technique or degree of crystallinity. A similar situation is seen for CeRhSb_{1-x}Sn_x, where CeRhSb is a Kondo semiconductor and CeRhSn exhibits NFL behavior.⁴⁷ In this system, it is possible to tune through a Kondo insulator - NFL quantum critical point as a function of dopant x. This situation may be analogous to the polycrystalline - single crystal CeRu₄As₁₂ weak insulator - NFL evolution where the tuning parameter is defect site or Ce concentration.

V. SUMMARY

It has been shown that measurements of $\rho(T)$, $\chi(T)$, $C(T)/T$, and $S(T)$ for single crystals of CeRu₄As₁₂ conform to NFL phenomena at low temperatures. Moreover, it appears that the Ce ions are in an intermediate valence state between 3⁺ and 4⁺, although this line of reasoning needs to be confirmed by x-ray absorption near - edge spectroscopy or measurements of the lattice constant to low T. As such, CeRu₄As₁₂ may be a member of a small class of quantum critical materials where a valence transition is central to the unusual behavior. By analogy to certain ternary Ce based compounds with the ThCr₂Si₂ structure (e.g., CeCu₂Si₂) and the CeRhSb_{1-x}Sn_x alloys, it appears that CeRu₄As₁₂ may have a complicated multi-dimensional phase diagram which includes an integral valence - intermediate valence phase transition and a metal - insulator transition. To test this premise, we plan

to explore the electronic state in $\text{CeRu}_4\text{As}_{12}$ as a function of pressure, magnetic field, and chemical substitution through electrical resistivity, specific heat, magnetization, and thermal transport measurements.

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TABLE I: Atomic coordinates, displacement parameters, and occupancy factors for CeRu₄As₁₂. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	$U_{eq}(\text{\AA}^2 \times 10^{-3})$	Occupancy Factor
Ru	0.25	0.25	0.25	3(1)	1.00(2)
As	0.1495(1)	0.3499(1)	0	4(1)	0.99(2)
Ce	0	0	0	11(1)	0.99(2)

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VII. TABLES AND FIGURES

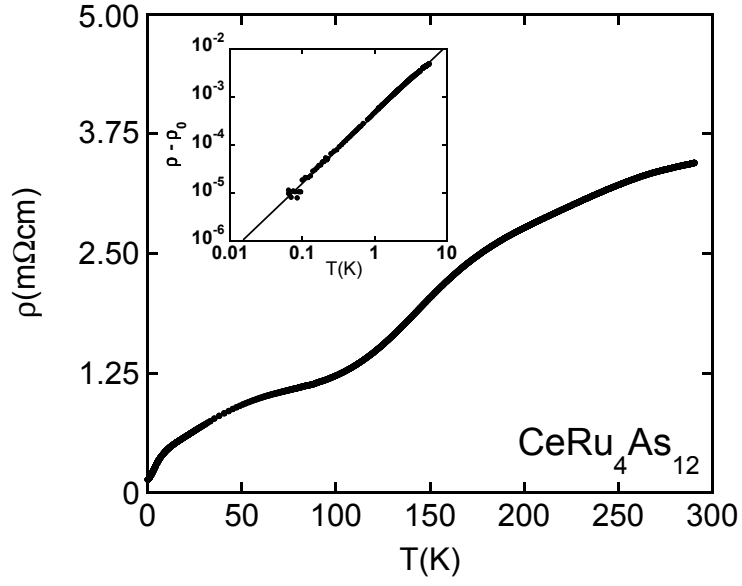


FIG. 1: Electrical resistivity ρ vs temperature T for CeRu₄As₁₂. Inset : log - log plot of $\rho - \rho_0$ vs T between 65 mK and 10 K, where ρ_0 is the residual resistivity. The data can be described by the expression $\rho(T) = \rho_0(1 + AT^n)$ with $\rho_0 = 136 \mu\Omega\text{cm}$, $A = 0.14 \text{ K}^{-n}$, and $n = 1.4$ (straight line in the figure).

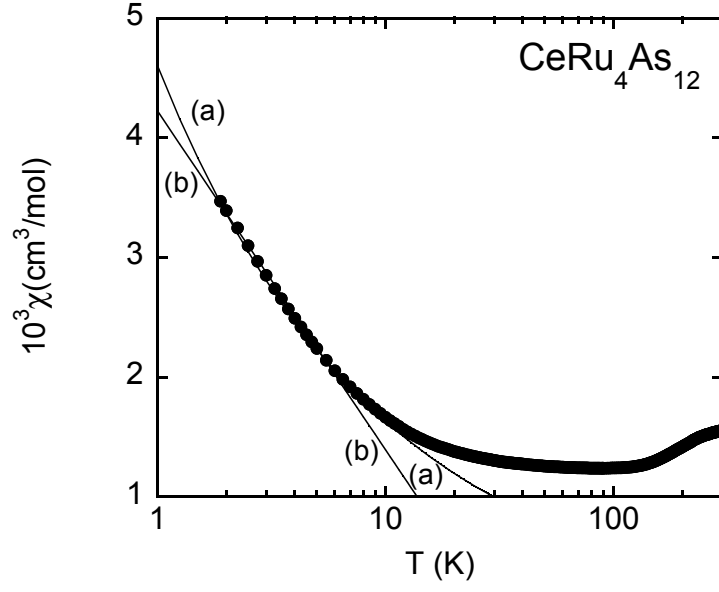


FIG. 2: Magnetic susceptibility χ vs temperature T for $\text{CeRu}_4\text{As}_{12}$ between 2 K and 300 K. For $2 \text{ K} < T < 10 \text{ K}$, $\chi(T)$ is described by either a power law function (curve a) or a logarithmic function (curve b) (see text).

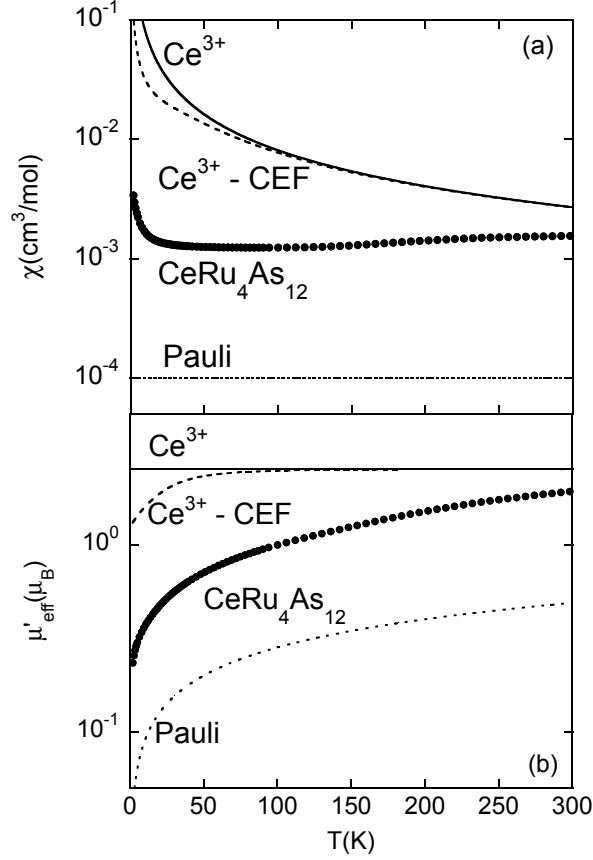


FIG. 3: (a) Magnetic susceptibility χ vs temperature T measured in a magnetic field $H = 10$ kOe for a $\text{CeRu}_4\text{As}_{12}$ mosaic compared to $\chi(T) = C/T$ where $C = N_A \mu_{\text{eff}}^2 / 3k_B$ and μ_{eff} is the Hund's rule multiplet value of $2.54 \mu_B$ for Ce^{3+} ions (curve " Ce^{3+} "), $\chi(T)$ for Ce^{3+} ions for which the crystalline electric field (CEF) splits the sixfold degenerate Hund's rule multiplet into a groundstate doublet and an excited state quartet with a splitting of 100 K (curve " $\text{Ce}^{3+} - \text{CEF}$ "), and a Pauli paramagnetic susceptibility of a typical metal appropriate for Ce^{4+} ions (curve "Pauli"). (b) The effective magnetic moment $\mu'_{\text{eff}} = \sqrt{\frac{3k_B \chi T}{N_A}}$ for the same cases described in panel a.

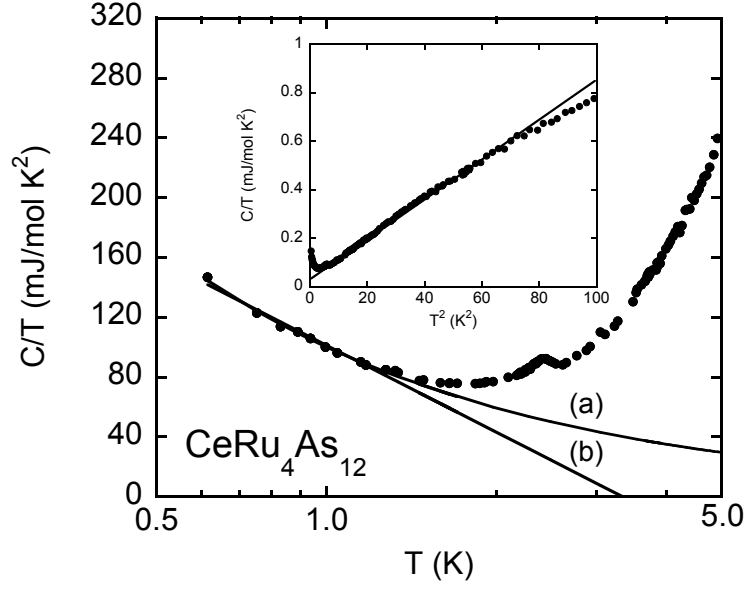


FIG. 4: Specific heat C divided by temperature T vs T for $\text{CeRu}_4\text{As}_{12}$. For $T < 2.6$ K, an upturn is observed which persists to 650 mK. The divergence conforms to a weak power law (curve a) or logarithmic function (curve b) (see text). It should be noted that a small feature is observed with a maximum at 2.4 K. Shown in the inset is a plot of C/T vs T^2 between 0.5 K and 10 K. The straight line is a fit of eq. 6 which yields $\gamma = 26$ mJ/mol K^2 and $\theta_D = 156$ K.

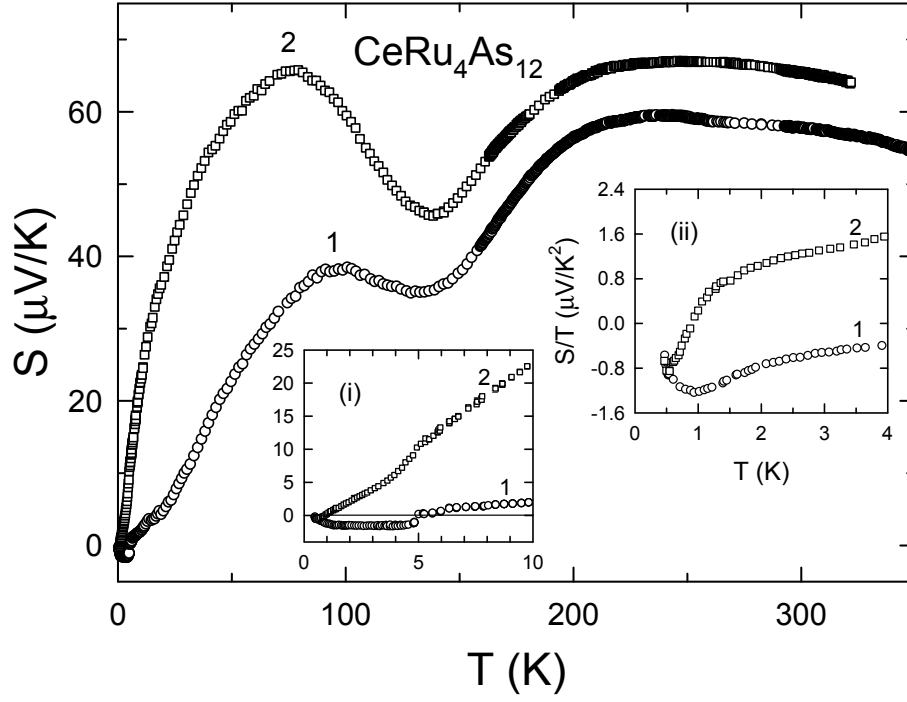


FIG. 5: Thermoelectric power S vs temperature T for two different crystals of $\text{CeRu}_4\text{As}_{12}$ from the same batch. Inset (i) shows S vs T between 0.47 K and 10 K while inset (ii) displays S/T vs T between 0.47 K and 4 K.